

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-105463

(43)Date of publication of application : 27.04.1993

(51)Int.Cl.

C03B 19/06  
A61K 6/027  
A61K 6/08  
A61L 27/00  
C03B 19/02  
C03C 10/02  
C03C 10/04

(21)Application number : 03-303944

(71)Applicant : NIPPON ELECTRIC GLASS CO LTD

(22)Date of filing : 22.10.1991

(72)Inventor : KOMATSUYA SHIYUNSUKE  
SHIBUYA TAKEHIRO

## (54) PRODUCTION OF CRYSTALLIZED GLASS

(57)Abstract:

PURPOSE: To produce crystallized glass by easy molding even in the case of a complex shape with high productivity without deteriorating characteristics such as mechanical strength.

CONSTITUTION: An  $\text{SiO}_2\text{-CaO-MgO}$  or  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO-MgO}$  type crystalline powdery glassy material is kneaded with an org. solvent such as methanol and a binder such as polyvinyl butyral to prepare a slip. This slip is cast with a casting mold having hygroscopic property such as a gypsum mold and the resulting casting is released from the mold, dried and sintered to obtain the objective crystallized glass having a desired shape.

## LEGAL STATUS

[Date of request for examination] 29.09.1998

[Date of sending the examiner's decision of rejection] 09.02.2001

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

\* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] The manufacture approach of the glass ceramics which knead an apatite, wollastonite and the crystalline glass powder that deposits at least one sort of a JIOPU side, and an organic solvent and a binder, produce a slip, carry out the slip casting of this slip using mold, and are characterized by sintering and crystallizing this crystalline glass powder while making a binder burned down by calcinating after unmolding and desiccation.

[Claim 2] The manufacture approach of the glass ceramics of claim 1 that an organic solvent is characterized by being a methanol, ethanol, propanol, butanols, or such mixture.

[Claim 3] The manufacture approach of the glass ceramics of claim 1 that a binder is characterized by being a polyvinyl butyral.

---

[Translation done.]

\* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of glass ceramics useful especially as biomedical materials about the manufacture approach of glass ceramics.

[0002]

[Description of the Prior Art] supplementation of the bone which suffered a loss conventionally -- a patient -- although the private bone extracted from his normal part has been used, in order to excise osseous tissues other than a damage part, in conducting that a patient's pain is large and an operation, by this approach, it has problems, like requiring a great effort and a limitation is in the output of a private bone.

[0003] To use the implant material artificially produced instead of the private bone from such a situation is tried. Glass ceramics, such as a  $\text{SiO}_2\text{-CaO-MgO}$  system and a  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO-MgO}$  system, are one of those which attract attention in these implant materials in recent years.

[0004] By the way, since crystallization takes place from a front face, if the above-mentioned glass ceramics carry out casting shaping of the melting glass, since a volumetric shrinkage happens in the case of subsequent crystallization and a crack occurs, they are not desirable. So, after grinding the crystalline glass usually fabricated in the shape of sheet metal, considering as the powder of 200 or less meshes and carrying out pressing of this by the rubber press method etc., this moldings is calcinated, glass powder is sintered and crystallized, and it is produced by carrying out cutting so that it may become a desired configuration further.

[0005]

[Problem(s) to be Solved by the Invention] However, in order for processing to take a great effort and time amount and for such an approach to take an advanced processing technique, the degree of freedom of the configuration by that productivity is low and processing has a limit, and since there are many a complicated configuration's being difficult to get and amounts of processings, it has problems, like a crack arises in glass ceramics and a mechanical strength tends to fall to them.

[0006] The purpose of this invention is offering the manufacture approach of the glass ceramics which can fabricate easily even if productivity's is a complicated high and configuration, and moreover do not spoil properties, such as a mechanical strength.

[0007]

[Means for Solving the Problem] The manufacture approach of the crystallization glass of this invention kneads an apatite, wollastonite and the crystalline glass powder that deposits at least one sort of a JIOPU side, and an organic solvent and a binder, produces a slip, carries out the slip casting of this slip using mold, and it is characterized by sintering and crystallizing this crystalline glass powder while making a binder burned down by calcinating after unmolding and desiccation.

[0008]

[Function] The crystalline glass used in the manufacture approach of the glass ceramics of this invention They are an apatite, wollastonite, and the thing that deposits at least one sort of a JIOPU side. For example, they are  $\text{SiO}_2$  40-60% and CaO at weight percent. 30 - 45%, The glass

which has the presentation of 1 - 17% of MgO(s) (however,  $\text{SiO}_2 + \text{CaO} + \text{MgO} \geq 90\%$ ),  $\text{SiO}_2$  22-50%,  $\text{P}_2\text{O}_5$  8-30%,  $\text{CaO}$  12 - 53%,  $\text{MgO}$  The glass which has 1 - 34% and F2 0-5% of presentation can be used. By making it crystallize, such crystalline glass has a high mechanical strength, and shows the outstanding living body activity and biocompatibility.

[0009] Next, the manufacture approach of the glass ceramics of this invention is explained.

[0010] First, the glass powder which has a presentation which was described above is kneaded with an organic solvent and a binder, and a slip is produced. 10 - 50% and 0.5 - 10% of the amount of mixing of an organic solvent and a binder is respectively desirable to 100 % of the weight of glass powder.

[0011] In addition, as for glass powder, it is desirable to use the thing of 200 or less meshes.

Moreover, since it will be eaten away if a water resisting property is bad and touches water, and a degree of sintering falls, the glass powder which has living body activity uses an organic solvent as a dispersion medium. It is desirable independent or that the dispersibility of glass powder uses alcohols, such as a good thing especially a methanol, ethanol, propanol, and a butanol, as an organic solvent, mixing. Although various things can be used as a binder, the polyvinyl butyral (PVB) excellent in especially the dispersibility of bonding strength or powder is desirable. In addition, an organic solvent and plasticizers other than a binder, such as a polyethylene glycol (PEG) and phthalic ester, may be added if needed.

[0012] Next, it unmolds, after carrying out a slip casting, putting an about [ ordinary pressure -10 kg/cm<sup>2</sup> ] pressure on the mold which has a desired configuration for the produced slip. In addition, what has hygroscopicity as mold to be used, for example, a plaster mold, a porosity plastic pattern, a biscuit mold, etc. are desirable.

[0013] While making a binder burned down by drying the Plastic solid furthermore acquired and calcinating, crystalline glass powder is sintered and crystallized and glass ceramics are obtained.

[0014]

[Example] Hereafter, based on an example and the example of a comparison, the manufacture approach of the glass ceramics of this invention is explained.

[0015] (Example) Table 1 and 2 shows the example of this invention.

[0016]

[Table 1]

(重量%)

試料No		1	2	3	4
ガラス組成	SiO <sub>2</sub>	52.5	55.0	48.2	50.5
	CaO	44.0	30.0	35.9	38.9
	MgO	3.5	15.0	6.8	7.1
	B <sub>2</sub> O <sub>3</sub>	—	—	4.5	—
	Al <sub>2</sub> O <sub>3</sub>	—	—	2.8	—
	Na <sub>2</sub> O	—	—	0.9	—
	K <sub>2</sub> O	—	—	0.9	—
	BaO	—	—	—	2.9
	F <sub>2</sub>	—	—	—	0.6
有機溶剤	メタノール	—	28	—	5
	エタノール	30	—	—	15
	プロパノール	—	—	—	10
	ブタノール	—	—	30	5
バインダー	PVB	0.5	3.0	1.0	5.0
可塑剤	PEG	1.0	—	—	—
	7カル酸エステル	—	—	1.5	—
曲げ強度 (kgf/cm <sup>2</sup> )		2300	2200	2100	2300

[0017]

[Table 2]

(重量%)

試料№		5	6	7	8
ガラス組成	SiO <sub>2</sub>	34.0	43.3	43.2	37.7
	P <sub>2</sub> O <sub>5</sub>	16.2	9.1	12.2	18.5
	CaO	44.7	36.5	31.4	14.5
	MgO	4.6	11.1	13.0	29.3
	F <sub>2</sub>	0.5	—	0.2	—
有機溶剤	エタノール	30	20	—	20
	プロパノール	—	10	—	—
	ブタノール	—	—	30	—
バインダー	PVB	2.0	0.5	1.5	1.0
可塑剤	PEG	—	—	—	1.0
	フタル酸エステル	—	—	—	1.0
曲げ強度 (kgf/cm <sup>2</sup> )		2400	2200	2600	2600

[0018] Sample No.1-8 were prepared as follows. Raw materials for glass were prepared so that it might become the presentation of front Naka, it put into platinum crucible, and after fusing for 4 hours and carrying out roll forming at 1400-1500 degrees C, the ball mill ground, it classified by the screen of 200 meshes, and crystalline glass powder was obtained. In addition, it kneaded with the ball mill for 24 hours at a rate which shows an organic solvent, a binder, and a plasticizer in a table to 100 % of the weight of this crystalline glass powder, and the slip was produced.

Subsequently, it is this slip to a plaster mold Ordinary pressure -10 kg/cm<sup>2</sup> It cast by the pressure, and unmolded after 3 - 60 minutes, and the Plastic solid with a magnitude of 4.5x3.4x41mm was acquired. After drying this Plastic solid furthermore, the temperature up was carried out in 1 hour at the rate of 30-300 degrees C, it calcinated at 1000-1200 degrees C for 2 to 10 hours, and the 4x3x36mm sample was obtained.

[0019] Thus, when asked for the deposit crystal of the obtained sample according to the X diffraction, sample No.1-4 deposited wollastonite and a JIOPU side, and sample No.5-8 deposited the apatite further.

[0020] Moreover, when the flexural strength of each sample was measured by the autograph, it is 2100 - 2600 kgf/cm<sup>2</sup>. The value was shown.

[0021] (Example of a comparison) The glass which has the same presentation as sample No.1 of an example, and 5 and 7 was ground, and it classified by the screen of 200 meshes, and considered as glass powder. Pressing of such glass powder was carried out by the rubber press method, respectively, and the Plastic solid with a magnitude of 50x50x120mm was acquired. Subsequently, by calcinating these Plastic solids at 1000-1200 degrees C for 2 to 10 hours, glass ceramics with a magnitude of 43x43x105mm were obtained. Furthermore, each glass ceramics were processed with the diamond cutter, and sample No.A with a magnitude of 4x3x36mm, and B and C were produced. Thus, as for the deposit crystal of each obtained sample, wollastonite and a JIOPU side, sample No.B, and C deposited [ sample No.A ] the apatite further.

[0022] next, the place which measured the flexural strength of each sample -- sample No.A --

2000 kgf/cm<sup>2</sup> and sample No.B -- 2200 kgf/cm<sup>2</sup> and sample No.C -- 2300 kgf/cm<sup>2</sup> it is -- as compared with sample No.1 manufactured by the approach of this invention, and 5 and 7, 300 kgf/cm<sup>2</sup>, 200 kgf/cm<sup>2</sup>, and 300 kgf/cm<sup>2</sup> were also low respectively.

[0023]

[Effect of the Invention] As explained above, even if it is glass ceramics with a complicated configuration, according to the manufacture approach of the glass ceramics of this invention, it can manufacture easily by using suitable mold. And since cutting is hardly needed, it is possible for properties, such as a mechanical strength, not to fall and to produce efficiently.

---

[Translation done.]